

Thermogravimetric and Kinetic Analysis of Co-Combustion of Waste Tires and Coal Blends

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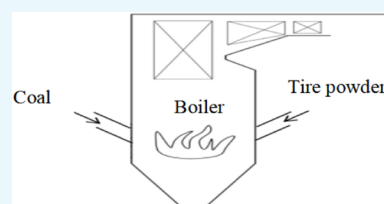


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ABSTRACT: The waste tire is a fuel with the potential to partially replace coal due to the high heat value. In the present study, the combustion characteristics of the tire powders, bituminous coal, and their blends were examined using the thermogravimetric analyzer. The influence of heating rate on tire powders combustion and the burnout characteristics of their blends were studied. The increase of the heating rate caused the combustion temperature of the tire powders to become high but reduced the maximum weight loss rate. The combustion characteristics of the blends of coal and tire powders approached the combination of those of the individual sample, suggesting that the interaction effects between coal and tire powders were slight. Furthermore, the influence of different ratios on ignition characteristics, burnout temperature, and combustion effect of the blends was studied at the optimal combustion rate. The addition of tire powders improved the ignition characteristics, reduced the burnout temperature and increased the burnout rate of coal to a certain extent. An increase in the proportion of tire powders led to a decrease in the activation energy in the temperature range of 349–465 °C, whereas it caused an increase from 465 °C to burnout, which could be attributed to the fact that the volatile matter was more combustible than fixed carbon within 349–465 °C, and the combustion effect of fixed carbon in the tire powders gradually manifested in the combustion from 465 °C to burnout when the tire powders content increased.



INTRODUCTION

With the rapid development of automobiles, about 1.5 billion tires are produced around the world every year, and the numbers keep growing with a high rate, resulting in severe challenges to the environment.¹ China, the European countries, the United States, Japan, and India produce the largest amount of waste tires, accounting for about 88% of the total.² China is a big tire producer whose production of waste tires ranks first in the world.³

Different from general solid waste, the properties of the waste tires, such as resistance to mechanical damage, abrasion resistance, water resistance, and nondegradability, make them very difficult to dispose of.^{4–8} It takes more than 100 years for microorganisms to decompose tires.⁹ Currently, the most common method for disposing of waste tires is stacking and burying in the open air,^{10,11} which easily cause fire or become a habitat for bacteria, threatening the safety and health of the people and environment.^{12–16} Therefore, there is an urgent need to explore effective methods to deal with waste tires.

Tires are mainly composed of synthetic rubber, natural rubber, carbon black, silica, and many additives; the carbon content of waste tires accounts for more than 80%.⁹ In addition, the moisture content of tires is extremely low compared with alternative energy such as municipal solid waste (MSW) or biomass. The calorific value of the tires reaches about 30–40 MJ/kg, which is higher than those of coal and other solid fuels.¹⁶ In the United States and some European countries, waste tires have been used as an alternative fuel

when blended with coal especially in the cement industry.¹ The cement plant ensures complete combustion of all parts of the tire because the temperature of the cement kiln is higher than 1200 °C.¹ Compared with coal combustion, tire combustion has lower emissions to ensure that its combustion in cement kilns is safe for the environment.^{17–20} Waste tires can also be used as fuel for the production of electricity, paper, lime, and steel because the co-combustion of waste tires and coal can improve the thermal efficiency of the boiler.¹⁴ Recently, researchers from various countries have conducted many experiments on the combustion of waste tires.^{21–32} Atal et al. compared the combustion behavior of coal and waste tire powder, and the effects of heating rate and particle size on combustion were also analyzed.²⁵ Sun et al. studied the pyrolysis characteristics of waste tires in an argon atmosphere for different pyrolysis gas, finding that the initial pyrolysis temperatures and maximum pyrolysis rates of waste tires increased with the increasing of heating rate, and the pyrolysis interval also shifted to high temperature.²⁶ Muelas et al. compared the combustion characteristics of tire pyrolysis

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liquid (TPL) with that of conventional hot oil (FO), including droplet and flame size evolution, burning rates, soot shell morphology, microexplosion occurrence, and soot analysis.²⁷ Prisciandaro et al. studied the pollutant emission properties of waste tires used in cement plant, which substantially meets the international standards.³⁰ Qu et al. adopted three isoconversional kinetic methods (Friedman's method, KAS method, and FWO method) to obtain the activation energy of waste tire in three circumstances (no catalyst, with ZSM-5, and with MnO_2).³¹ In reviewing recent studies concerning the reactions of waste tires, it is noted that few research studies have been carried out to examine the co-combustion of waste tires and coal blends, even though numerous studies have been performed on waste tires. For this reason, the present study aims to investigate the combustion characteristics and combustion kinetics of waste tires and coal blends. The waste tire is mixed with coal in various weight ratios. The mixtures are burned in a non-isothermal environment, and thermogravimetric analysis is carried out. The co-combustion and kinetics of the blends are then explained in detail.

RESULTS AND DISCUSSION

Combustion Characteristics of Individual Sample. As shown in Figure 1a, the TGA curve of pure coal indicates that

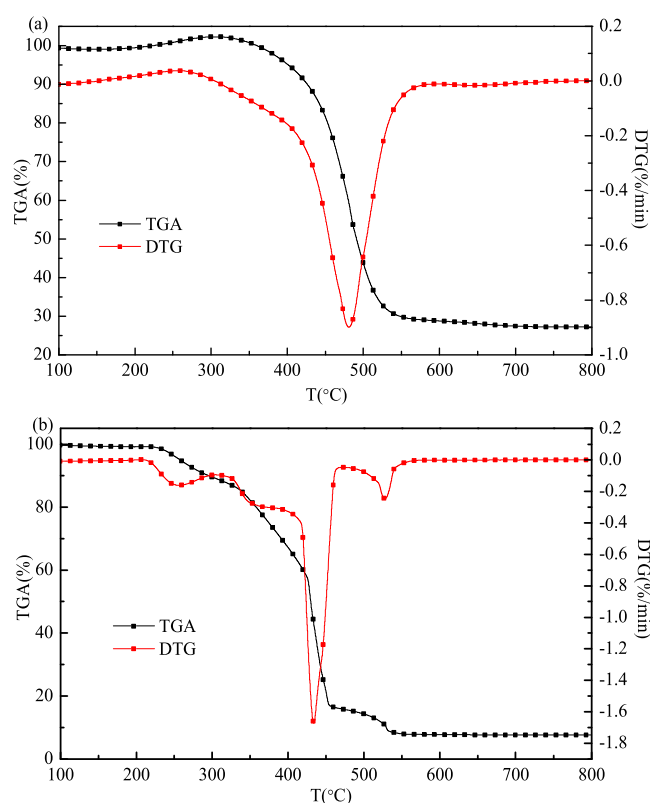


Figure 1. TGA and DTG curves of (a) coal (b) tire powders.

the weight loss is mainly caused by the combustion of volatile matter and fixed carbon with a weight loss rate of 72.79%. Different from coal, there are four obvious weight loss processes of tire powders as shown in Figure 1b, which are caused by volatile matter release, combustion, and fixed-carbon combustion. The corresponding weight loss rates are 13.24, 29.52, 40.12, and 9.47%, respectively. Compared with the derivative thermogravimetric (DTG) curves in Figure 1, a

significant weight loss process is only observed in the temperature range of 400–560 °C, which may be caused by the burning of volatile matter and fixed carbon.³³ It means that pure coal combustion has only one maximum reaction rate. However, the combustible components in tire powders are precipitated at low temperatures, with the presence of four obvious weight loss rate change areas in the DTG curve. The weight loss process is mainly concentrated in the release and combustion stages of volatiles, such as hydrocarbons, carbon oxides, and hydrogen. The steep peaks in DTG indicate that the volatile matter of tire powders are released and burned rapidly. There are three obvious peaks located at 250.74, 354.63, and 427.66 °C in the DTG curve of tire powders, which may be caused by the release and combustion of different volatile substances.³⁴ The fourth temperature peak at 529.71 °C may be formed by the combustion of fixed carbon, which is higher than the peak temperature of coal (481.26 °C). The volatile matter released in the tire powders hinders the contact between oxygen and fixed carbon, although its combustion also consumes a large amount of oxygen around the particles. Only when the volatile matter is almost burned out, the fixed carbon starts to burn with the condition of contact with oxygen at a sufficiently high temperature.

Effect of Heating Rate. Figures 2 and 3 show the combustion characteristic curves of tire powders at the heating

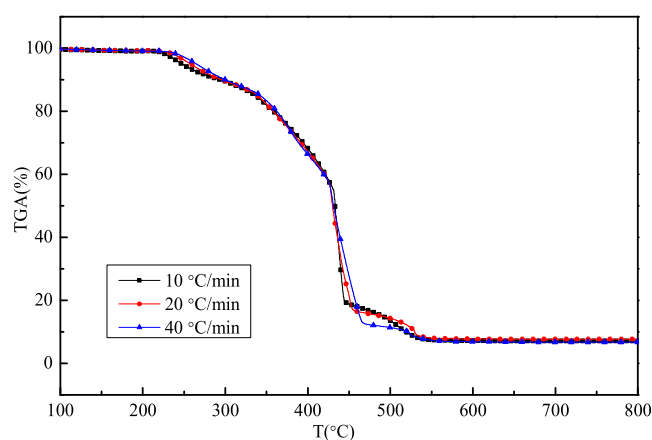


Figure 2. TGA curves of tire powders at different heating rates.

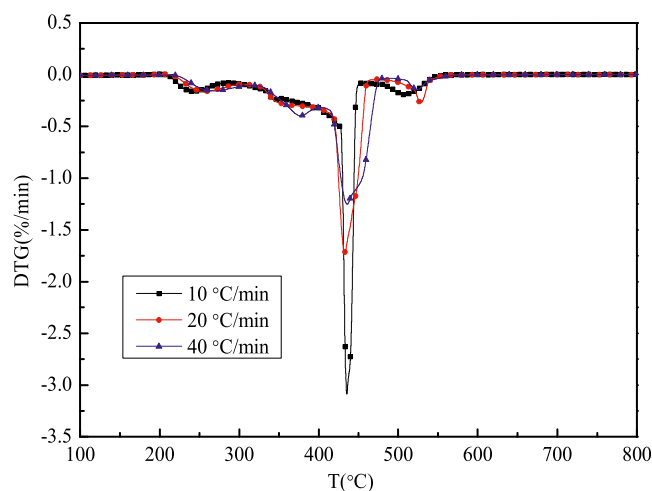


Figure 3. DTG curves of tire powders at different heating rates.

rates of 10, 20, and 40 °C/min. The analysis shows that the heating rate has a significant effect on the combustion characteristics of the tire powders. It can be observed from Figure 2 that the temperature at which weight loss begins is gradually delayed with the increase of the heating rate. The curve moves to the high-temperature zone, but the final combustion efficiency is little affected by the increase of the heating rate. The DTG curve of Figure 3 shows that the weight loss rate corresponding to the peak decreases as the heating rate increases. The linear heating process shortens the time for the sample with a larger heating rate to reach the set temperature, which indicates that the combustion reaction time is also shortened. When the heating rate is large, the sample has a low weight loss rate due to insufficient burning time, causing the maximum weight loss rate to decrease with the increase in the heating rate.³⁵

Combustion Characteristics of Blends. *Combustion Process of Process.* It can be observed from Figure 4 that the

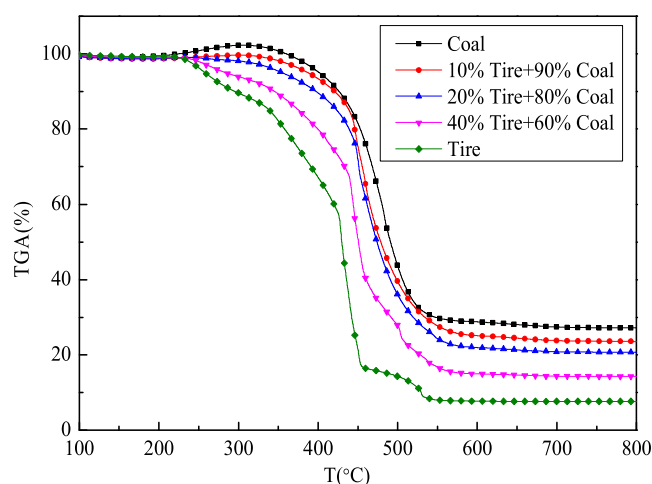


Figure 4. TGA curves of different proportions of blends.

TGA curves shift to the right as the ratio of the coal increases. It means that the required temperature rises as the ratio of coal powders increases under the same weightlessness. Moreover, the increase in the proportion of coal leads to a significant change in the final weight loss rate, which is mainly caused by the different ash content in coal and tire powders. The DTG curves calculated by the TGA experiment in Figure 5 shows that the peak value of the individual samples is basically reflected in the curves of mixture combustion, which indicates that the interaction effects between coal and tire powders are slight.

Combustion Parameters of Blends. As can be observed from Table 1, the ignition temperature of tire powders is 349.71 °C, which is 83.74 °C lower than that of coal. Compared with the coal, the ignition temperature of the sample is reduced by 9.34, 22.59, and 62.76 °C when the sample is mixed with 10, 20, and 40% tire powders, respectively. It means that the increasing ratio of tire powders decreases the ignition temperature of the sample. This is principally because a large amount of volatile matter in the tire powders releases and burns quickly under low-temperature conditions, improving the ignition performance of coal. Besides, when the ratio of tire powders is higher, the burnout temperature and the weight of solid residue (η) are lower at the end of the combustion reaction. Therefore, it is inferred

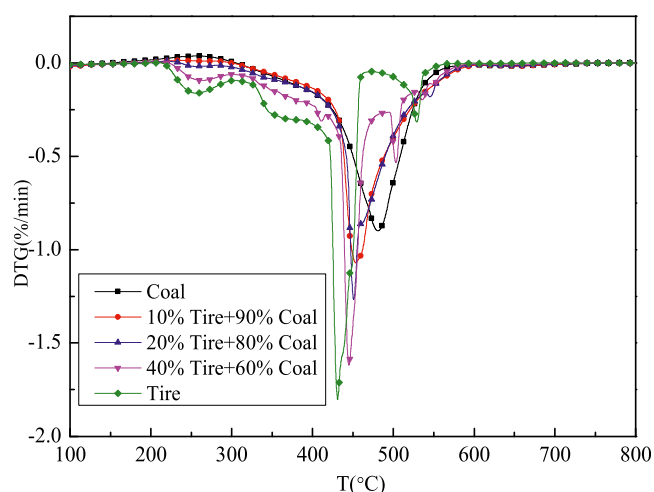


Figure 5. TGA curves of different proportions of blends.

Table 1. Combustion Characteristic Parameters of the Samples

sample	T_i (°C)	T_f (°C)	η (%)
tire	349.71	562.84	5.63
40% tire + 60% coal	370.69	580.05	13.28
20% tire + 80% coal	410.86	593.20	18.69
10% tire + 90% coal	424.11	601.12	21.57
coal	433.45	613.31	25.21

that the addition of tire powders can increase the burnout rate and reduce the burnout temperature of coal.

Combustion Kinetic Analysis. There are different reaction processes in the combustion of tire powders (i.e., volatile matters combustion and fixed-carbon combustion process). The TGA curves given in Figure 1b suggest that the reaction intensity of the two combustion processes is quite different. Therefore, the combustion kinetics of tire powders needs to be studied in two temperature ranges. The activation energies and the pre-exponential factors of the samples are listed in Table 2. Meanwhile, the linear regression for the

Table 2. Combustion Kinetic Parameters of the Samples

sample	T (°C)	E_a (kJ/mol)	A (min^{-1})	R^2
tire	349–465	38.13	1.14×10^2	1.00
	465–563	85.69	5.42×10^5	0.95
10% tire + 90% coal	424–465	76.20	4.37×10^4	0.99
	465–601	45.26	4.50×10^2	0.94
20% tire + 80% coal	411–465	62.76	4.62×10^3	0.95
	465–593	55.90	2.71×10^3	0.96
40% tire + 60% coal	371–465	42.80	1.80×10^2	0.98
	465–580	63.71	1.15×10^4	0.95
coal	433–613	92.92	7.29×10^6	0.96

extraction of the kinetic parameters of the blend of 40 wt % tire powders + 60 wt % coal in two temperature ranges is presented in Figure 6. The value of R^2 in the two temperature ranges is greater than 0.94, indicating that the two-stage combustion process has a good correlation.³⁶ When the proportion of tire powders in the blends increases, the activation energy and pre-exponential factor values in the temperature range of 349–465 °C show a decreasing trend. Accounting for the combustion of volatile components, the reactivity of volatile components is

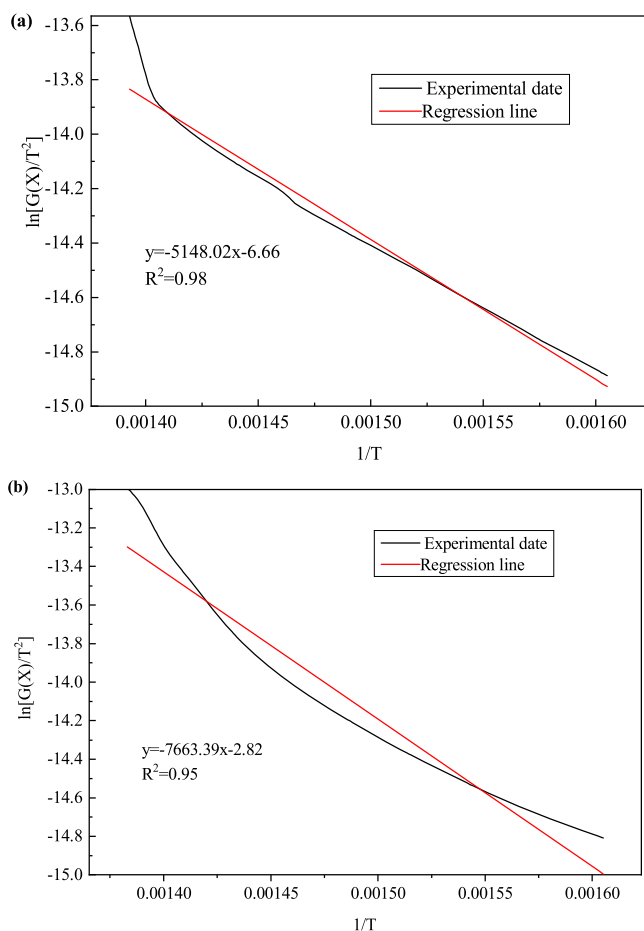


Figure 6. Linear regression for the extraction of the kinetic parameters of the sample of 40 wt % tire + 60 wt % coal at (a) temperature range of 371–465 °C and (b) temperature range of 465–580 °C.

less than that of fixed carbon, and this is the reason why the activation energy and pre-exponential factor rise when the proportion of tire powders goes down. From 465 °C to burnout, the combustion effect of fixed carbon in the tire powders gradually manifests in the combustion of the blends as its proportion increases, resulting in the combustion kinetic parameters of the blends gradually tending to that of the tire powders.^{35,37}

CONCLUSIONS

The combustion characteristics of the tire powder and bituminous coal, as well as the co-combustion of their blends, have been examined in the present study through thermogravimetric analyses. The results show that the combustion process of tire powders includes the release and combustion of a large amount of volatile matter and combustion of fixed carbon. The increase of the heating rate causes the combustion temperature of the tire powders to become high but reduces the maximum

weight loss rate. However, it has little effect on the final combustion efficiency. The results of the analyses indicate that the combustion characteristics of the blends of coal and tire powders approach the combination of those of the individual sample. Thus, it is concluded that the interaction effects between coal and tire powders are only slight. The addition of tire powders improves the ignition characteristics, reduces the burnout temperature, and increases the burnout rate of coal to a certain extent. An examination of the combustion kinetics of the samples shows that an increase in the ratio of tire powders leads to a decrease in the activation energy in the temperature range of 349–465 °C, whereas an increase from 465 °C to burnout arising from that the combustion of volatile components the combustion effect of fixed carbon in the tire powders gradually manifests in the combustion from 465 °C to burnout when the tire powders content increases. Generally, the combustion kinetic parameters of the blends gradually tends to that of the tire powders as the increase of ratio of tire powders.

MATERIALS AND METHODS

Materials. Truck tire powders with a particle size of about 26 mesh and bituminous coal, which was ground with a particle size similar to that of tire powders, were used in the experiments. The mixture of the tire powders and coal was dried in an oven at 363 K for 4 h. The blending ratios of waste tire to bituminous coal with values of 0, 10, 20, 40, and 100 wt % were taken into consideration in our study.

The proximate and ultimate analysis results of the samples were conducted according to GB/T 212-201 (2001) and GB/T 476-2001 (2001), respectively. As shown in Table 3, the property analysis results for bituminous coal and waste tires revealed that the carbon content and calorific value of waste tires are higher than that of coal, but the moisture, sulfur, and nitrogen contents get lower. In addition, the ash content of the tire is very low, making the treatment of the ash more convenient.

Thermogravimetric Analysis. A thermogravimetric analyzer (TGA/DSC-2 1600lf) was used to examine the combustion characteristics of the samples in this study. A ceramic crucible containing the sample (10 mg) was located in the TG, where the weight of the sample was constantly monitored. The experiment was performed in an oxygen atmosphere at a flow rate of 20 mL/min with the temperature ranging from ambient temperature to 800 °C with the heating rate of 10, 20, and 40 °C/min. The experiment for each sample was repeated three times to ensure reproducibility.

The TGA–DTG method was used to determine the ignition point in this study, as shown in Figure 7.³⁸ Through the peak point M on DTG, a vertical line was drawn upward to reach the TGA curve at point N. A tangent line to the TGA curve through point N was drawn, which intersected the initial level line of the TGA curve at point O. A vertical line going down through point O was drawn, intersecting the abscissa at point

Table 3. Properties of Bituminous Coal and Waste Tire

sample	proximate analysis (wt %, air-dried basis)				elemental analysis (wt %, air-dried basis)					high heat value (MJ/kg)
	M_{ad}	V_{ad}	A_{ad}	FC_{ad}	C	H	O	N	S	
coal	9.58	34.13	21.28	35.01	73.10	5.52	8.67	1.45	1.68	29.31
tire	0.60	61.19	5.64	32.57	82.57	6.42	7.88	0.60	1.93	34.70

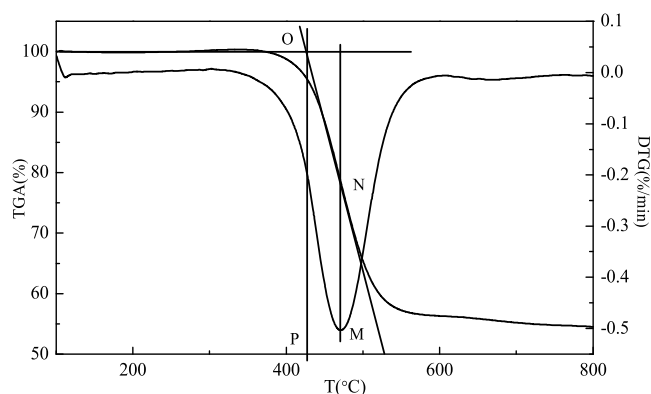


Figure 7. Ignition point (T_i) definition diagram.

P. The ignition point corresponded to the temperature point D, which could be defined as T_i

Kinetic Methods. In general, the kinetic expression of solid combustion is³⁹

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

where t is the time, min, and α is the fuel conversion rate, defined as follows

$$\alpha = \frac{W_i - W}{W_i - W_f} \quad (2)$$

where W_i , W , and W_f represent the instantaneous, initial, and final mass of the sample, respectively.

k is the reaction rate constant expressed by the Arrhenius equation

$$k = A \exp(-E_a/RT) \quad (3)$$

where R is the gas constant with a value of 8.314 J/(K·mol); E_a is the activation energy, KJ/mol; A is the pre-exponential factor; and T is the reaction temperature, K.

The function $f(\alpha)$ can be written as follows

$$f(\alpha) = (1 - \alpha)^n \quad (4)$$

Substituting eqs 3 and 4 into eq 1, we can get the following expression

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right)(1 - \alpha)^n \quad (5)$$

Given the constant heating rate equation $\beta = dT/dt$, eq 5 can be rewritten as follows

$$\frac{dX}{dt} = \left(\frac{1}{\beta}\right) A \exp\left(\frac{-E_a}{RT}\right)(1 - \alpha)^n \quad (6)$$

Ordering $n = 1$ ^{13,40} and using the integration method of the Coats and Redfern (CR) equations and eq 6,^{41–43} we get an equation as follows

$$\ln\left[-\frac{(1 - \alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E_a}\left(1 - \frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \quad (7)$$

For most reactions, the value of $2RT/E_a$ is very small ($2RT/E_a \ll 1$), so $\ln\left[-\frac{(1 - \alpha)}{T^2}\right]$ has a linear relationship with $1/T$.

Making $a = -E_a/R$, $b = \ln\left[\frac{AR}{\beta E_a}\left(1 - \frac{2RT}{E_a}\right)\right]$, $Y = \ln[T^2 - \ln(1 - \alpha)]$, the equation can be described as

$$Y = b + ax \quad (8)$$

The values of the activation energy (E_a) and pre-exponential factor (A) are determined by the values of a and b .

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Notes

The authors declare no competing financial interest.

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